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(19) **United States**(12) **Patent Application Publication****Balmer-Millar et al.**(10) **Pub. No.: US 2003/0118960 A1**(43) **Pub. Date: Jun. 26, 2003**(54) **LEAN NOX AFTERTREATMENT SYSTEM****Publication Classification**

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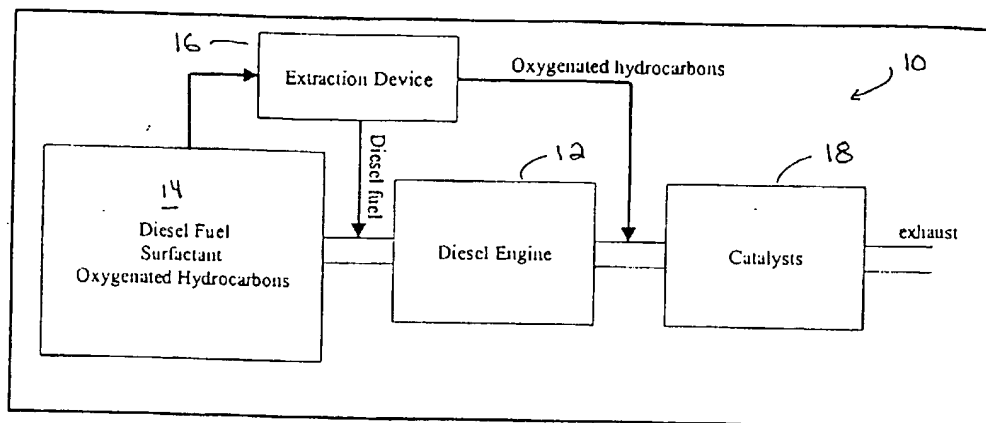
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**ABSTRACT**

A lean NO<sub>x</sub> aftertreatment system is disclosed. The lean NO<sub>x</sub> aftertreatment system includes a fuel source having oxygenated hydrocarbons homogeneously dispersed therein, a reductant extraction subsystem adapted for extracting the oxygenated hydrocarbons from the fuel, and a high performance lean NO<sub>x</sub> catalyst. The disclosed lean NO<sub>x</sub> catalyst is a metal or metal oxide doped alumina based catalyst (or other oxide material), wherein the metal or metal oxide dopant may be selected from the group consisting of indium, gallium, tin, silver, germanium, gold, nickel, cobalt, copper, iron, manganese, molybdenum, chromium, cerium, vanadium, oxides thereof, and combinations thereof.

(21) Appl. No.: **10/177,458**(22) Filed: **Jun. 21, 2002****Related U.S. Application Data**

(60) Provisional application No. 60/344,939, filed on Dec. 21, 2001.



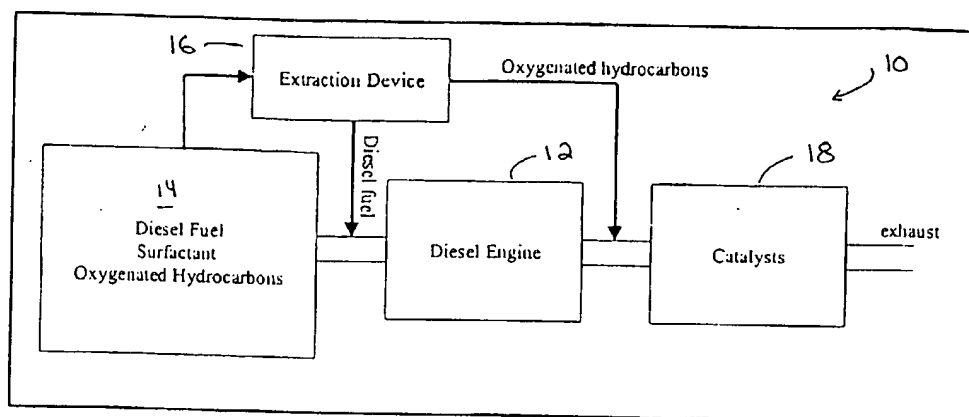


FIG. 1

## LEAN NO<sub>x</sub> AFTERTREATMENT SYSTEM

[0001] This application claims the benefit of prior provisional patent application Serial No. 60/344,939 filed Dec. 21, 2001.

### Technical Field

[0002] This invention relates generally to a lean NO<sub>x</sub> aftertreatment system for treatment of engine exhaust to reduce nitrogen oxide (NO<sub>x</sub>) emissions and more specifically to a system that provides for the combination of selected oxygenated hydrocarbons with metal or metal oxide doped alumina catalysts to achieve high NO<sub>x</sub> reduction from engine exhaust.

### BACKGROUND

[0003] Due primarily to federal regulations, engine manufacturers are being forced to reduce the amount of regulated emissions in the combustion exhaust, including a reduction in nitrogen oxides or NO<sub>x</sub>. To effectively reduce the NO<sub>x</sub> concentrations in the exhaust stream of lean burning engines including diesel and certain spark ignited engines, the use of selective catalytic reduction of NO<sub>x</sub> with a hydrocarbon reductant in oxygen rich conditions (lean NO<sub>x</sub> catalyst systems) is actively being pursued.

[0004] There is an abundance of prior art in the field of lean NO<sub>x</sub> catalysts and catalyst systems. Unfortunately, many catalysts or catalytic systems that have been utilized for lean burn engines to date suffer from inadequate performance, including low removal of NO<sub>x</sub>, inadequate catalyst durability, low thermal stability and a limited temperature window of operation. For example most commercially available lean NO<sub>x</sub> catalytic systems for lean burn engines only achieve less than 20% NO<sub>x</sub> reduction as a passive system and possibly up to 40% (i.e. when supplemental hydrocarbon reductant such as diesel fuel is introduced into the exhaust stream). In addition, most commercially available lean NO<sub>x</sub> catalytic systems also are subjected to sulfur and phosphorous poisoning, from the minimal amounts of sulfur found in many fuels and lubrication oils as well as hydro-thermal sintering, resulting in low catalyst durability.

[0005] Active catalytic systems involving lean NO<sub>x</sub> catalysts require a sufficient concentration of hydrocarbon (HC) species to be present in the exhaust. In other words, in combustion exhaust purification systems having an oxygen environment above 4% concentration, some type of reducing agent, usually a hydrocarbon compound such as diesel fuel, must be introduced into the exhaust in order to achieve acceptable reduction levels of NO<sub>x</sub> compounds. However, such introduction of fuel tends to reduce the overall fuel efficiency of the engine system.

[0006] The use of other reductants, such as ethanol, may address some of the NO<sub>x</sub> reduction performance issues for such lean NO<sub>x</sub> catalysts. However, there is presently no infrastructure in place to commercially provide alternative reductants, such as ethanol, to the many mobile applications that are in need of such lean NO<sub>x</sub> catalyst systems. In addition, it is not practical from a cost effective, space, and anti-defeat viewpoint, to design mobile applications that require both a primary fuel for combustion and a separate secondary reductant for aftertreatment purposes. Also, lean

NO<sub>x</sub> catalyst development could be further optimized for aftertreatment systems using other reductants such as ethanol or other oxygenated hydrocarbons.

[0007] What is needed therefore, is a commercially practical lean NO<sub>x</sub> catalyst system for predominately mobile applications that optimizes the physical and chemical properties of a lean NO<sub>x</sub> catalyst as well as provides of the most suitable partially oxidized hydrocarbon reductant for the catalytic reactions.

[0008] The lean NO<sub>x</sub> catalyst system should preferably utilize the same source of fuel used for engine combustion and should demonstrate good selectivity of both NO and NO<sub>2</sub> in order to achieve both an improvement in the reduction of NO<sub>x</sub> from the engine exhaust stream while minimizing the fuel efficiency and cost impact on the overall mobile system. The presently disclosed lean NO<sub>x</sub> catalyst system is directed to overcome one or more of the problems as set forth above.

### SUMMARY OF THE INVENTION

[0009] The present invention may be characterized as a lean NO<sub>x</sub> aftertreatment system comprising a fuel source having oxygenated hydrocarbons dispersed therein, a reductant extraction subsystem adapted for extracting the oxygenated hydrocarbons from the fuel, and a lean NO<sub>x</sub> catalyst. The lean NO<sub>x</sub> catalyst may include a metal or metal oxide doped alumina based catalyst (or other oxide material), wherein the metal or metal oxide dopant may be selected from the group consisting of indium, gallium, tin, silver, germanium, gold, nickel, cobalt, copper, iron, manganese, molybdenum, chromium, cerium, vanadium, oxides thereof, and combinations thereof.

### BRIEF DESCRIPTION OF THE DRAWINGS

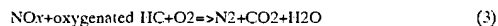
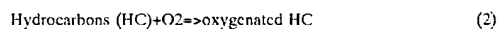
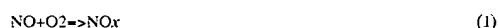
[0010] The above and other aspects, features and advantages of the present lean NO<sub>x</sub> catalyst will be more apparent from the following more particular description thereof, presented in conjunction with the following drawings, wherein

[0011] FIG. 1 is a schematic diagram of a lean NO<sub>x</sub> aftertreatment system in accordance with the present embodiments of the invention.

### DETAILED DESCRIPTION

[0012] The following description is of the best mode presently contemplated for carrying out the invention. This description is not to be taken in a limiting sense but is made merely for the purpose of describing the general principals of the invention. The scope and breadth of the invention should be determined with reference to the claims.

[0013] Although the lean-NO<sub>x</sub> catalytic reaction is a complex process comprising many steps, one of reaction mechanisms for lean NO<sub>x</sub> catalysts can be summarized as follows:



[0014] Since certain oxide catalysts have been known to activate the NO<sub>x</sub> reduction step summarized in equation (3), the embodiments disclosed herein focus on combinations of specific oxygenated hydrocarbons with specific oxide based

catalysts (e.g. metal/metal oxide doped alumina). These metal or metal oxide doped alumina material more readily catalyze the reaction of NO<sub>x</sub> with oxygenated hydrocarbons as well as demonstrate improved thermal stability, and therefore improve the overall NO<sub>x</sub> reduction performance of the lean NO<sub>x</sub> catalyst. The presently disclosed embodiments and examples demonstrate that the physical and chemical properties of an alumina, or other oxide based catalyst materials, in combination with selected oxygenated hydrocarbons determine the overall catalytic performance of the lean NO<sub>x</sub> catalyst system, including NO<sub>x</sub> reduction performance as well as catalyst durability and temperature based performance of the lean NO<sub>x</sub> catalyst system.

[0015] FIG. 1 provides a schematic diagram of a lean NO<sub>x</sub> aftertreatment system 10 coupled to a "lean burn" engine 12, shown in FIG. 1 as a diesel engine. Throughout the specification and the claims, however, a lean burn engine is defined as one that produces an oxygen rich exhaust, which is defined as an exhaust having a higher molar ratio of oxygen than the total molar ratio of reductive compounds such as carbon-monoxide, hydrogen, hydrocarbons, and oxygenated hydrocarbons. The exhausts have an oxidative environment. Examples of such lean burn engine systems include diesel engine systems; some natural gas or alternative fuel engine systems; liquid or gaseous-fueled turbine engines; and various lean burn gasoline engine systems. Generally, diesel engine systems, as shown in FIG. 1, generate an exhaust having an oxygen content of from 4% to 16% depending on the load conditions and the running mode of the diesel engine.

[0016] The depicted lean NO<sub>x</sub> aftertreatment system 10 of FIG. 1 may include a fuel source 14 having oxygenated hydrocarbons dispersed therein; a reductant extraction subsystem 16 adapted for extracting the oxygenated hydrocarbons from the fuel source 14; and a lean NO<sub>x</sub> catalyst 18 adapted to reduce NO<sub>x</sub> from the engine exhaust with the aid of the oxygenated hydrocarbons. Each of the elements of the disclosed lean NO<sub>x</sub> aftertreatment system 10 may be operatively and/or physically coupled to the diesel engine 12. For example, the fuel source 14 not only provides the source of oxygenated hydrocarbons for the lean NO<sub>x</sub> aftertreatment system 10, but also provides the primary source of fuel for combustion within the engine, and is thus coupled to the engine 12. Likewise, the lean NO<sub>x</sub> catalyst 18 is also coupled to the engine 12 such that exhaust gases created during the combustion are directed to the lean NO<sub>x</sub> catalyst 18. It is also contemplated that any controls for the lean NO<sub>x</sub> aftertreatment system 10, including controls for the reductant extraction subsystem 16 (e.g. extraction and injection of the oxygenated hydrocarbons), controls for the thermal management and flow control within the lean NO<sub>x</sub> aftertreatment system 10, and other system controls may be integrated with the engine control module (ECM).

[0017] The fuel source 14 preferably may include a base hydrocarbon such as diesel fuel, gasoline, or an alternative fuel (e.g. bio-diesel or fuel blended emulsions); oxygenated hydrocarbons; and a surfactant or other additive package adapted to keep the oxygenated hydrocarbons homogeneously dispersed in the base hydrocarbon. Other additives, such as lubricity enhancers, corrosion inhibitors, cetane improvers, may also be included in the fuel source depending on the application in which the system may be intended.

[0018] The oxygenated hydrocarbons may be alcohols, aldehydes, and ketones, or combinations thereof. More preferably, the oxygenated hydrocarbons may include the following: methanol, ethanol, propanol, butanol, pentanol, hexanol, methanal, ethanal, propanal, butanal, propenal, acetone, 2-butanone, and 3-penten-2-one.

[0019] The reductant extraction subsystem 16 is a system or device adapted for extracting the oxygenated hydrocarbons from within the fuel source. Contemplated embodiments of the reductant extraction subsystem may include a heating unit adapted to distill the oxygenated hydrocarbons from a portion of the fuel source 14. Alternatively, a non-thermal plasma-based system may be employed as reductant extraction subsystem 16 to create the necessary or desired oxygenated hydrocarbons from the fuel source 14. Yet another contemplated embodiment of the reductant extraction subsystem 16 is a fuel reformer or reactor such as a millisecond reactor, suitable for use in a mobile application, that produces the desired oxygenated hydrocarbons from a portion or small sample of the fuel source 14. As indicated above, the preferred fuel source may be diesel fuel or gasoline, and the preferred oxygenated hydrocarbons produced by such reformer may be alcohols, aldehydes or ketones.

[0020] In the illustrated embodiment, the oxygenated hydrocarbons produced from the reductant extraction subsystem may be introduced in the exhaust stream from the diesel engine 12 at a location downstream of the engine cylinders and upstream of the lean NO<sub>x</sub> catalyst using an auxiliary injector (not shown) that preferably may be controlled by the engine control module (ECM).

[0021] The preferred lean NO<sub>x</sub> catalyst 18 may be a metal or metal oxide doped alumina catalyst wherein the metal or metal oxide promoters (i.e. the active ingredients) are selected from the group consisting of indium, gallium, tin, silver, germanium, gold, nickel, cobalt, copper, iron, manganese, molybdenum, chromium, cerium, vanadium, oxides thereof, and any combinations thereof. The combination can be a homogeneous mixture or layered catalytic material in which the exhaust stream passes through a first catalyst bed and then through a second catalyst bed.

[0022] The lean NO<sub>x</sub> catalyst 18 preferably possess the customized physical and chemical characteristics, disclosed hereinafter, that yield both high NO<sub>x</sub> reduction performance as well as other advantageous lean NO<sub>x</sub> catalyst performance characteristics, such as durability, resistance to sulfur and phosphorous poisoning, and thermal stability. The preparation and preferred composition of the preferred lean NO<sub>x</sub> catalysts as well as the catalytic reactions are described more fully below.

#### [0023] Lean NO<sub>x</sub> Catalyst Preparation

[0024] In the present embodiments of the lean NO<sub>x</sub> aftertreatment system a metal doped, oxide catalyst is used. The metal doped, oxide catalyst includes a substrate, an oxide support material, and active metal or metal oxide promoters or dopants. The lean NO<sub>x</sub> catalyst is prepared by coating the substrate with an oxide support material. The substrate is preferably a ceramic honeycomb or metallic substrate, the composition of which is preferably selected from the group consisting of cordierite, alumina, titania, and FeCr alloy, although other suitable substrates can also be used.

[0025] Preferably, the oxide support material is an alumina, but alternate oxide support materials may also be considered, including aluminophosphates, hexaluminates, aluminosilicates, zirconates, gallium oxides, titanosilicates, and titanates. Still further, it is even more preferred that  $\gamma$ -alumina support material be utilized for optimized performance of the lean NO<sub>x</sub> catalyst. As described herein, preparation of the washcoat oxide material is preferably accomplished using techniques such as various sol-gel processes so as to precisely control the physical and chemical characteristics of the oxide support material, including the characteristics of pore size, pore volume, surface area, concentration of impurities and thermal stabilizers. Conventional precipitation techniques can be used to prepare the desired  $\gamma$ -alumina if one or more of the aforementioned characteristics are met. The oxide support material is then applied to the substrate or monolith in a manner to achieve a uniform catalyst coating on such substrate or monolith. The oxide coated substrate then undergoes controlled calcination to remove many unwanted and volatile components.

[0026] Next, various metal or metal oxide promoters are introduced or doped into the oxide-coated substrates. The active ingredient (i.e. metal/metal oxide promoters) loading and metal or metal oxide dispersion, or metal species particle size are also precisely controlled for optimized performance of the lean NO<sub>x</sub> catalyst and to optimize other catalyst performance characteristics such as sulfur tolerance (i.e. resistance to sulfur poisoning) and temperature based performance. The preferred metal promoters include indium, gallium, tin, silver, germanium, gold, nickel, cobalt, copper, iron, manganese, molybdenum, chromium, cerium, vanadium, and the oxides thereof, and combinations thereof. More preferably the use of metal promoters indium, gallium, silver and tin (or the oxides thereof) and combinations thereof including homogeneous mixtures or layered structure, have resulted in good overall catalyst performance, including NO<sub>x</sub> reduction performance. Surface area, pore size, and pore volume measurements

[0027] The surface area, pore volume, and pore size distribution of various catalyst samples may be determined using a Micromeritics ASAP 2000 system. Approximately 0.2 to 2 grams of catalyst may be preferably out gassed under vacuum at 450° C. overnight prior to adsorption measurements. The surface area may then be determined by multipoints measurement using several relative pressures of N<sub>2</sub> to He in the range of 0.06 to 0.2 (N<sub>2</sub> surface area 0.162 nm<sup>2</sup>) at 77K.

#### [0028] Impurity Content Measurements

[0029] The level of impurity in various catalyst samples may be determined using ICP analysis. The ICP analysis may be performed using a Jobin Yvon 48 instrument. The catalyst samples may be completely digested in acid (HF) and diluted with de-ionized water. The acid solution may be injected into the plasma and the Jobin Yvon 48 instrument may then scan the samples for all the elements including sulfur.

#### [0030] Formation of Oxide Support Material by a Sol-Gel Process

[0031] It has been found that oxide catalyst formed by a sol-gel method produces an oxide support material having unique properties for utilization in lean NO<sub>x</sub> catalytic treat-

ment of oxygen rich exhaust. Various methods of forming the oxide support materials were investigated. In one embodiment,  $\gamma$ -alumina was prepared by a complexing agent assisted, sol-gel method. Another embodiment had the  $\gamma$ -alumina support material prepared by sol-gel method without the use of a complexing agent.

[0032] In the complexing agent assisted, sol-gel method aluminum isopropoxide (AIP) (98+%, Aldrich Chemical Company, Inc.) was dissolved in 2-methyl-2,4-pentanediol (MPD) (99% Aldrich Chemical Company, Inc.). First, 500 g AIP was placed in a 2-liter glass beaker and then 600 milliliters of MPD was added immediately and the mixture was stirred vigorously with a mechanical polyethylene stirrer. Once the mixture was homogeneous, the beaker was placed in a constant temperature bath at a range of from 110 to 130° C. and stirred continuously. After approximately 1 hour of stirring, all of the AIP was dissolved in the MPD. As the AIP reacts with the MPD, it produces 2-propanol which is released as a vapor at these temperatures. Gelation was completed after approximately 4 hours of reaction. Then 400 milliliters of water were added to stop the gelation and a white precipitate of aluminum hydroxide was obtained. The aluminum hydroxide solid was re-dispersed in water and aged at a temperature of from 60 to 90° C. overnight with constant stirring.

[0033] After aging overnight, about 600 milliliters of 2-propanol was added to remove the water from the pores of the precipitate. Although 2-propanol or methanol is preferred, any organic solvent having a surface tension of approximately equal to or less than 30 mN/m will be useful. It is just necessary that the solvent have a surface tension significantly below that of water, which is approximately 72 mN/m. The resulting slurry was vacuum filtered and dried at approximately 90° C. in an oven for 48 hours.

[0034] Calcination was carried out in a temperature programmed tube furnace with 5 L/min air flowing through it. A general calcination schedule is as follows: ramp the temperature from 100° C. to a maximum temperature of about 600° C. to 700° C. at about 1° C. to 2° C. per minute; maintain at the maximum temperature for a prescribed time; and turn off the heat and continue flowing air over the alumina until the temperature is reduced to 100° C. During calcinations, a selected amount of water (e.g. between about 2% and 6% or more) can be added to partially sinter the powders.

[0035] This sol-gel procedure may be controlled so as to yield  $\gamma$ -alumina with surface areas between about 80 m<sup>2</sup>/g and 350 m<sup>2</sup>/g and more preferably greater than approximately 200 m<sup>2</sup>/g. This sol-gel procedure may also be controlled so as to yield  $\gamma$ -alumina with pore volumes of between about 0.5 to 2.0 cc/g, and pore sizes averaging of between about 3 to 30 nm.

[0036] Transmission Electron Microscopy (TEM) images of the  $\gamma$ -alumina prepared using the sol-gel technique revealed a needle-shape morphology of the  $\gamma$ -alumina. The  $\gamma$ -alumina needle morphology observed had relatively short and rounded features. On average, the needle size was about 1-10 nm wide and 20-50 nm long. In addition, these particles were polycrystalline according X-ray diffraction patterns. These features are a result of the  $\gamma$ -alumina having been prepared using the complexing agent MPD. The MPD is considered a strong complexing agent that results in short-rounded alumina particles.

[0037] As indicated above, alternate embodiments of  $\gamma$ -alumina may be prepared using a sol-gel method without using a complexing agent. This procedure may involve preparing a white slurry consisting of amorphous aluminum hydroxide by mixing aluminum isopropoxide with an excess of hot water at approximately 80° C. under vigorous stirring conditions. The white slurry may be subsequently washed with water or organic solvents such as 2-propanol or methanol. In addition, it may be advantageous to add a small amount of nitric acid or other solution to control the pH of the resulting alumina. The alumina sol-gel may then be dried at approximately 90° C. overnight and calcined, as generally described above, in a temperature-programmed furnace with a flowing air atmosphere.

**[0038] Metal or Metal Oxide Doping of Oxide Support Material**

[0039] The metal or metal oxide doping of the alumina or oxide support material can be preferably accomplished in one of two ways. In one method, the subject metal or metal oxide dopant is solubilized in the water that is used to stop gelation during the sol-gel procedure described above.

[0040] In a second method, the calcined sol-gel oxide support material (e.g.  $\gamma$ -alumina) may be doped with a metal or metal oxide by an incipient wetness impregnation method. In the preferred incipient wetness impregnation method, the calcined powder sol-gel prepared  $\gamma$ -alumina may be brought into contact with a solution of the appropriate metal. The solution of the metal or metal oxide may be present in an amount equal to or greater than the total pore volume of the  $\gamma$ -alumina sample. The pore volume of  $\gamma$ -alumina preferably may be between about 0.5 and about 2.0 cc/g of alumina. Broadly speaking, the alumina wash-coated substrates may be dipped into solutions prepared with precursors of the active ingredient (i.e. metal or metal oxides) such as nitrates, acetates, chlorides, carbonates, and sulfates. This process may be controlled in order to provide the desired active ingredient concentrations as well as the desired interactions between the active ingredient and the washcoated alumina and to control the desired pH of the solution.

[0041] To form an indium or indium oxide doped  $\gamma$ -alumina by the incipient wetness method an appropriate amount of  $\text{In}(\text{NO}_3)_3$  (or  $\text{InCl}_3$ ) may be dissolved in a water solution and brought into contact with the sol-gel  $\gamma$ -alumina. The indium or indium oxide doped  $\gamma$ -alumina catalyst may then be calcined at 600° C. for about 5 hours. Indium or indium oxide loading of  $\gamma$ -alumina catalyst may be in the range of between about 1 weight percent and about 10 weight percent, with a more preferable indium or indium oxide loading percentage being approximately 2.5 weight percent.

[0042] Tin or tin oxide doped  $\gamma$ -alumina may be prepared in the same manner using  $\text{SnCl}_3$  in an ethanol solution instead of water. The tin or tin oxide doped  $\gamma$ -alumina catalyst may be calcined at 600° C. for about 5 hours and then at 800° C. for about 2 hours. Tin or tin oxide loading of  $\gamma$ -alumina catalyst is preferably in the range of between about 1 weight percent and 20 weight percent, with a more preferable tin or tin oxide loading being about 10 weight percent.

[0043] A third promising metal promoter may be gallium or gallium oxide. A gallium or gallium oxide doped  $\gamma$ -alu-

mina may be prepared by exposing the  $\gamma$ -alumina to a water solution of  $\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$  which was added to the aluminum oxide gel during the  $\gamma$ -alumina preparation in the sol-gel method. The gallium or gallium oxide doped  $\gamma$ -alumina catalyst may be calcined at 600° C. for about 5 hours to form oxides of gallium loaded alumina. Gallium or gallium oxide loading of the  $\gamma$ -alumina catalyst may be in the range of between about 1 weight percent and about 55 weight percent, with a more preferable gallium or gallium oxide loading percentage being approximately 5 to 35 weight percent.

[0044] To form a silver doped  $\gamma$ -alumina catalyst by the incipient wetness method an appropriate amount of silver nitrite may be dissolved in a water solution and brought into contact with the sol-gel  $\gamma$ -alumina. The silver doped catalyst may be prepared using the same procedure as described above with tin and gallium doped catalysts. The silver doped catalyst is preferably calcined at about 600° C. for about 5 hours to form oxides of silver loaded alumina. Silver loading of the  $\gamma$ -alumina catalyst may be in the range of between about 1 weight percent and about 10 weight percent, with a more preferable silver loading percentage being approximately 2 to 6 weight percent.

[0045] Based on the analysis of various testing data, including that data disclosed in U.S. patent application Ser. Nos. 09/999,999 and 09/999,998, both filed on Dec. 18, 2001, the disclosures of which are incorporated by reference, it has been found that various oxide support materials suitable for use in a lean NOx aftertreatment system should preferably include one or more physical characteristics. For example, the alumina support material may preferably have a pore volume of from between about 0.5 to approximately 2.0 cubic centimeters per gram, and more preferably 1.0 to 1.5 cubic centimeters per gram, as well as an impurity level and/or thermal stability additive level of less than or equal to 0.2 weight percent. Likewise, the surface area of the oxide support material, such as alumina, to be used in a lean NOx aftertreatment system may vary between about 80 m<sup>2</sup>/g and 350 m<sup>2</sup>/g, but it is preferable that the surface area be equal to or greater than 200 m<sup>2</sup>/g. Also the acidity level of the alumina or other oxide support material can be controlled to optimize the operating temperature window and associated fuel penalty realized by such lean NOx catalyst. The pH of the MPD solution used in the aforementioned processes is preferably in the range of about 8.0 to 10.0.

#### INDUSTRIAL APPLICABILITY

[0046] As indicated above, the embodiments disclosed herein may be characterized as lean NOx aftertreatment systems comprising a fuel source having oxygenated hydrocarbons dispersed therein, a reductant extraction subsystem adapted for extracting the oxygenated hydrocarbons, such as alcohols, aldehydes, and ketones from the fuel source, and a high performance lean NOx catalyst. As previously disclosed, the lean NOx catalyst may include a metal or metal oxide doped alumina based catalyst (or other oxide material), wherein the metal or metal oxide dopant may be selected from the group consisting of indium, gallium, tin, and silver, and oxides thereof, and combinations thereof. It is fully contemplated however, that other metal or metal oxide promoters such as germanium, gold, nickel, cobalt, copper, iron, manganese, molybdenum, chromium, cerium, vanadium could also be utilized in the lean NOx catalyst.

[0047] Although the present invention may be used in most any application requiring a lean NOx aftertreatment system, it is envisioned that the catalyst disclosed herein is best suited for use in a lean NOx exhaust aftertreatment system for mobile applications, such as on-highway, off-highway, and marine diesel engines. Advantageously, the present invention does not require both a primary fuel for combustion and a separate secondary reductant for aftertreatment purposes. Rather, a single fuel source is utilized to for both combustion within the engine as well as for the aftertreatment system. In addition, the fuel reforming or other oxygenated hydrocarbon extraction subsystem yields the desired oxygenated hydrocarbon from the primary source of fuel. In this manner, the optimized lean NOx catalytic reaction may be facilitated with selected alcohols, aldehydes, and ketones and selected metal or metal oxide doped catalysts.

[0048] From the foregoing, it can be seen that the disclosed embodiments provide a metal-doped oxide catalyst for lean NOx aftertreatment system and method for preparing the same. While the embodiments herein disclosed has been described by means of specific materials and methods or processes associated therewith, numerous changes, modifications, and variations could be made thereto by those skilled in the art without departing from the scope of the invention as set forth in the claims.

What is claimed is:

1. A lean NOx aftertreatment system comprising:
  - a fuel source having oxygenated hydrocarbons dispersed therein;
  - a reductant extraction subsystem adapted for extracting the oxygenated hydrocarbons from the fuel;
  - a lean NOx catalyst including a substrate, an oxide support material deposited on the substrate, and a metal or metal oxide dopant selected from the group consisting of indium, gallium, tin, silver, germanium, gold, nickel, cobalt, copper, iron, manganese, molybdenum, chromium, cerium, vanadium, oxides thereof, and combinations thereof.
2. The lean NOx aftertreatment system of claim 1 wherein the oxygenated hydrocarbon is selected from the group of methanol, ethanol, propanol, butanol, pentanol, and hexanol.
3. The lean NOx aftertreatment system of claim 1 wherein the oxygenated hydrocarbon is selected from the group of methanol, ethanal, propanal, propenal, and butanal.
4. The lean NOx aftertreatment system of claim 1 wherein the oxygenated hydrocarbon is selected from the group of acetone, 2-butanone, and 3-penten-2-one.
5. The lean NOx aftertreatment system of claim 1 wherein the fuel source is diesel fuel.
6. The lean NOx aftertreatment system of claim 1 wherein the fuel source is gasoline.
7. The lean NOx aftertreatment system of claim 1 wherein the fuel source includes: a base hydrocarbon selected from the group consisting of diesel fuel and gasoline; an oxygenated hydrocarbon selected from the group consisting of alcohols, aldehydes, and ketones; and a surfactant adapted to keep the oxygenated hydrocarbons dispersed in the base hydrocarbon.
8. The lean NOx aftertreatment system of claim 1 wherein the reductant extraction subsystem adapted for extracting the

oxygenated hydrocarbons from the fuel is a heating unit adapted to distill the oxygenated hydrocarbon from the fuel source.

9. The lean NOx aftertreatment system of claim 1 wherein the reductant extraction subsystem is a reactor that is suitable for fuel reformation and to yield alcohols, aldehydes or ketones.

10. The lean NOx aftertreatment system of claim 1 further comprising a reductant injection system.

11. The lean NOx aftertreatment system of claim 1 wherein the oxide support material is  $\gamma$ -alumina.

12. The lean NOx aftertreatment system of claim 1 wherein the oxide support material is prepared using a sol-gel method.

13. The lean NOx aftertreatment system of claim 12 wherein the oxide support material is prepared using a sol-gel method assisted with a complexing agent.

14. The lean NOx aftertreatment system of claim 13 wherein the complexing agent is 2-methyl-2,4-pentanediol (MPD).

15. The lean NOx aftertreatment system of claim 1 wherein the oxide support material is prepared from materials in the group consisting of aluminophosphates, zirconates, hexaluminates, aluminosilicates, titanosilicates, and titanates.

16. The lean NOx aftertreatment system of claim 1 wherein the metal or metal oxide dopant includes indium or indium oxide, and the lean NOx catalyst having an active ingredient loading of between about 1 weight percent and 10 weight percent.

17. The lean NOx aftertreatment system of claim 16 wherein the metal or metal oxide dopant includes indium or indium oxide, and the lean NOx catalyst having an active ingredient loading of about 2.5 weight percent.

18. The lean NOx aftertreatment system of claim 1 wherein the metal or metal oxide dopant includes gallium or gallium oxide, and the lean NOx catalyst having an active ingredient loading of between about 1 weight percent and 55 weight percent.

19. The lean NOx aftertreatment system of claim 18 wherein the metal or metal oxide dopant includes gallium or gallium oxide, and the lean NOx catalyst having an active ingredient loading of greater than 5 weight percent.

20. The lean NOx aftertreatment system of claim 1 wherein the metal or metal oxide dopant is tin or tin oxide, and the lean NOx catalyst having an active ingredient loading of between about 1 weight percent and 20 weight percent.

21. The lean NOx aftertreatment of claim 20 wherein the metal or metal oxide dopant is tin or tin oxide, and the lean NOx catalyst having an active ingredient loading of about 10 weight percent.

22. The lean NOx aftertreatment system of claim 1 wherein the metal or metal oxide dopant is silver, and the lean NOx catalyst having an active ingredient loading of between about 1 weight percent and 10 weight percent.

23. The lean NOx aftertreatment of claim 22 wherein the metal or metal oxide dopant is silver, and the lean NOx catalyst having an active ingredient loading of about between about 2 weight percent and 6 weight percent.

24. The lean NOx aftertreatment of claim 11 wherein the alumina support material has a surface area of between about 80 m<sup>2</sup>/g and 350 m<sup>2</sup>/g.

25. The lean NOx aftertreatment of claim 24 wherein the alumina support material has a surface area of greater than about 200 m<sup>2</sup>/g.

26. The lean NOx aftertreatment of claim 11 wherein the alumina support material has an average pore size of between about 8 nm and 30 nm in diameter.

27. The lean NOx aftertreatment of claim 26 wherein the alumina support material has an average pore size of greater than about 12 nm in diameter.

28. The lean NOx aftertreatment system of claim 1 wherein the oxide support material contains silicon in the amount of about 0.1 weight percent or less.

29. The lean NOx aftertreatment system of claim 1 wherein the oxide support material contains sodium oxide in the amount of about 0.1 weight percent or less.

30. The lean NOx aftertreatment system of claim 1 wherein the oxide support material contains sulfates in the amount of about 0.1 weight percent or less.

31. The lean NOx aftertreatment system of claim 11 wherein the alumina support material has a pore volume of between about 0.5 to 2.0 cc/g.

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